

SOME FURTHER CONSIDERATIONS IN THE DEVELOPMENT OF THE ELECTRON CONCEPTION OF VALENCE.

By K. GEORGE FALK.

(Read April 24, 1914.)

The electron conception of valence is based upon the view that when two atoms combine, one becomes charged positively and the other negatively. According to J. J. Thomson,<sup>1</sup> the union of two atoms is brought about by the transfer of a negatively charged corpuscle from one atom to the other; the atom losing the corpuscle becoming charged positively, the one gaining the corpuscle, charged negatively. In order to represent graphically the linkings between atoms the lines or dots which represent the bonds ordinarily are replaced by arrows in the electronic considerations, the head of the arrow indicating the direction in which the corpuscle is assumed to be transferred in the production of the chemical bond.

In every discussion of valence, it is necessary to consider the limitations of the problem. Valence is a number. The valence of an atom shows the number of corpuscles or negative electrons gained or lost by that atom in forming chemical bonds. In slightly different terms, the valence of an atom shows the number of atoms (or groups of atoms) held in combination by that atom when the hydrogen atom as it exists in most of its compounds is taken as the positive unit. Valence may be likened to the capacity factor in energy considerations.<sup>2</sup> Like the capacity factor, it is denoted by a definite number, and while this number may vary under different conditions, a quantity or number of atoms (or combining weights) held by an atom (or combining weight) of the element in question is always meant.

<sup>1</sup> "The Corpuscular Theory of Matter," pp. 138-9 (1907).

<sup>2</sup> Cf. S. L. Bigelow, "Theoretical and Physical Chemistry," p. 80 (1913).

In the same way, the chemical affinity between two combining atoms would correspond to the intensity factor in chemical energy. This chemical affinity can be measured quantitatively only by the change in free energy of the reaction in question. Stability relationships, or chemical affinity discussions, do not enter directly into valence questions, although the existence of substances is controlled entirely by these. The separation of these two problems, valence and chemical affinity, makes it clear that while a great number of substances may be predicted from a consideration of valence structures alone, questions of chemical affinity, or relative stability, limits the number of these substances which are actually known or may be prepared.

As a result of the comparative study of large numbers of compounds, it has become possible to say which would probably exist under ordinary conditions and whether some would react more rapidly than others. These qualitative factors do not give any information concerning the real quantitative measures of relative stability.

Valence is therefore essentially a classifying principle. While it is based directly upon and derived from the atomic theory, it may also be used without considering atoms. The conception of atoms and molecules is based upon the experimental laws of definite and multiple proportions, and if, instead of atoms and molecules, combining and formula weights are used, the same relations will be found, although perhaps not pictured as readily.

The most important feature of the present development is that in speaking of the valence of an element, it is not sufficient to give a number. It is just as important to state whether this number is positive or negative, as the valence or the number of unit atoms or groups held in combination involves also the question whether these are electropositive or electronegative. This is brought out clearly in the Periodic System of Mendeléeff, especially for Groups 4 to 7, where the types of combination with hydrogen and with oxygen represent the maximum negative and positive valences of the elements of these groups.

Since the valence of an atom may be positive or negative depend-

ing upon the loss or gain of corpuscles, the knowledge of the electrical state of an atom in a compound is of importance. Ionization in solution is an invaluable aid in determining the distribution of these charges. Dissolving a substance does not produce electric charges on atoms but only makes these charges manifest to certain experimental methods. These are, in fact, the only direct experimental methods for determining valence. For substances which ordinarily do not ionize, a knowledge of the distribution of the charges is also important. This question was taken up for organic compounds and reactions by Professor J. M. Nelson, of Columbia University and the speaker in a number of papers.<sup>3</sup> It was shown that satisfactory classifications could be developed with the electron conception of valence alone, but that the use of both polar and non-polar valences leads to contradictions in reactions which are fundamentally similar.

With compounds which do not ionize, the Periodic System serves in a general way as a guide for developing valence structures in which relative positive and negative properties of the different atoms are involved. When two atoms are united by a single bond (one unit of valence), where one corpuscle is transferred in the production of the bond, there is ordinarily no question of the direction of transference of this corpuscle, that is to say, which element is positive and which is negative. If isomers exist, the difference in the relative affinity of the atoms for the negative corpuscle may be small (as in iodine monochloride) and the less stable modification may possess the structure in which the corpuscle is transferred in the opposite direction from that of the stable modification.

Some interesting questions are raised when the double bond is considered from the electronic point of view. As used in the past, the justification for the double bond lies in the desire to maintain consistently, constant values for the valence of certain atoms. Practical work during the past fifty years has borne out within certain limits the usefulness of this conception. Before discussing the significance of the double bond with the newer ideas of valence, some general

<sup>3</sup> *Jour. Amer. Chem. Soc.*, 32, 1167 (1910); 33, 440 (1911); 35, 1810 (1913); 36, 209 (1914).

facts must be mentioned. A single bond between two atoms gives no information as to the stability of the union between these atoms. A double bond between two atoms cannot give any more information with regard to the stability of the linking. Qualitatively it has been found that the rate of reaction for compounds containing double bonds is greater in some ways than the rate for compounds containing single bonds, and that with certain reagents decomposition at the double bond occurs more rapidly than at other parts of the molecule, but this is manifestly different from a discussion of true stabilities of compounds. Reaction velocities bear no simple relation to stabilities of substances and "reactivity" as used in organic chemistry very often refers only to these reaction velocities. The double bond in the ordinary language signifies two units of valences just as the single bond denotes one unit of valence, and in this sense, the only permissible one, the representation of a double bond by two lines is a correct picture of the linking when one line is used for the single bond.

When two atoms of elements which differ very markedly in electrochemical properties are combined by a double bond, one of these atoms may be considered to be electropositive and the other electronegative. In valence terms, an atom of one of these elements has given up two negative electrons to the atom of the other to form the double bond, the former becoming positive, the latter negative. These cases are as simple as those in which only single bonds are involved. Two units of valence are used in each linking with the result that the valence of one of the atoms is  $+2$  and of the other  $-2$  due to the double bond.

If two atoms of elements which do not differ much in electrochemical properties are combined by a double bond, the possible relations from the electronic point of view are somewhat more complex. On the other hand, explanations of reactions and classifications of isomers are afforded which are not possible with the view of the double bond in which electrons are not considered.

For the present purpose, it will be sufficient to outline some of the relations. The substances to be considered include mainly the compounds of carbon with double bonds between two carbon atoms

or between one carbon atom and an atom of some other element such as oxygen or nitrogen. In order to illustrate the present discussion with a definite case, a compound containing a double bond between two carbon atoms in which the other bonds are combined with similar groups, may be chosen. Two possible arrangements suggest themselves with regard to the directions in which the corpuscles may be transferred to form the double bond. One carbon atom may lose two corpuscles and the other may gain two in the formation of the double bond. In this case, the valence of the first carbon atom due to the double bond is  $+2$ , of the second  $-2$ . The other possibility involves the gain and loss of one corpuscle by each of the carbon atoms in forming the double bond. In this case, the valence of each carbon atom due to the double bond will be  $-1 + 1$ . Since the oxidation of an atom is defined as a decrease of the negative charge or number of corpuscles, and reduction as a decrease of the positive charge, these atoms united by the double bond would be present in different states of oxidation in the different isomeric substances. It is evident therefore, that, with the electron conception, the double bond may show different reactions with various reagents depending upon the directions of the valences of the double bond or the state of oxidation of the atoms united by the double bond. Isomeric substances might exist in which the isomerism would be due to the different directions of the valences of the double bond. This subject has been discussed at some length in previous papers.<sup>4</sup>

Similar relations should be expected to hold with compounds containing a triple bond. While not as much work has been recorded in the literature for substances of this nature, it has been possible, with the electron conception of valence, to explain some reactions of compounds containing triple bonds much more satisfactorily than with the older valence view.

The general view of valence is that of a classification of chemical compounds and reactions. Since the introduction of the electronic nature of valence into all branches of chemistry widens and

<sup>4</sup>Cf. *S. of M. Quarterly*, 30, 179 (1909); *Jour. Amer. Chem. Soc.*, 32, 1167 (1910).

extends the classification, and since much of the classification depends upon a number of correlated facts and relations and not upon single crucial and well-defined experiments, it may be expected that some of the formulas advanced and explanations of reactions offered at the present time will be subject to change. Caution must continually be exercised against reading into valence structures ideas which are foreign to valence. A limitation of the questions discussed to the phenomena which may rightly be included would obviate much confusion and bring valence relations into clearer light.

HARRIMAN RESEARCH LABORATORY,  
ROOSEVELT HOSPITAL, NEW YORK.